



National Institute of Oceanography and Fisheries
Egyptian Journal of Aquatic Research

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FULL LENGTH ARTICLE

Sodium diethyldithiocarbamate as accelerator of the rate of copper cementation



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Received 13 May 2015; revised 30 August 2015; accepted 30 August 2015

Available online 21 October 2015

KEYWORDS

Cementation of copper;
 Zinc;
 Mass transfer;
 Sodium
 diethyldithiocarbamate

Abstract The effects of Cu^{2+} ion concentration and temperature on the cementation rate of copper from copper sulphate on zinc and the effect of additives of the organic compound “sodium diethyldithiocarbamate” (NaDDC) were studied. It was noticed that the cementation increases significantly by increasing the concentrations of NaDDC. The rate of cementation increased by 58.58–100.31%. Our data showed that sodium diethyldithiocarbamate reacts with the Cu^{2+} solution giving a complex of copper diethyldithiocarbamate, which enhances the rate of cementation. © 2015 National Institute of Oceanography and Fisheries. Hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Introduction

Since copper metal is insoluble, most copper included in the water system is in the form of copper salts (e.g., copper sulphate, etc.). Such salts are used in electroplating industry, engraving, and photography/photos development. Wastes from rinse tanks and filter clean out also find their way into the sanitary system (Dickinson, 1974). Copper ions, as a pollutant, do not accumulate in the human body but if they are taken in massive amounts can cause illness or even death.

Soluble Cu salts wastes are of particular concern because of their high degree of toxicity to aquatic organisms. The principal sources of soluble copper salts wastes have been identified as: (1) the cleaning water output from the electroplating industry; (2) aching solution wastes from printed circuit production;

(3) spent Cu catalysts; (4) copper pickling liquor; and (5) the cleaning wastewater output from the textile industry. The concentration of copper ions in the wastes should not exceed 1.5 ppm (Taha, 2004).

Cementation process is a precipitation process where metal ions precipitated from anthropogenic sources of metals (Larry Benefield, 1976), such as copper sulphate on a cathode made from another metal, such as zinc, by electrochemical process. This process is usually used in electroplating industry from many years ago, and also for wastewater purification (Mubarak et al., 2004; Agelidis et al., 1985; Strickland and Lawson, 1973; Makhoulfi et al., 2000). Cementation reaction is a heterogeneous process limited by the diffusion through the mass boundary layer. The cementation rate does not only depend on the prevailing hydrodynamic conditions, but also on the nature of the deposited metal; powdery non-coherent deposits may increase the cementation rate while smooth coherent deposits may forbid the cementation process (Biswas and Davenport, 1980; Gould et al., 1984; Mackinnon et al., 1971).

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Peer review under responsibility of National Institute of Oceanography and Fisheries.

<http://dx.doi.org/10.1016/j.ejar.2015.08.002>

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The removal of heavy metals especially Cu^{2+} by cementation has been studied by a number of researchers who used different less noble metals such as Zn, Fe and Al and different methods to enhance the rate of cementation such as the rotating disk (Zaghib et al., 1990, 1997), the rotating cylinder (Biswas and Reid, 1972), agitated vessels (Nosier, 2003), gas sparging (Noseir, 2010) fixed and fluidized beds (Ahmed, 2011) and surface pulsation (Agarwal and Mines, 1988). In most of the cases, the cementation reactions from dilute solutions have been found to follow first-order diffusion controlled kinetics (Konsowa, 2010).

The aim of the present work is to investigate the effect of the organic compound sodium diethyldithiocarbamate on the rate of copper cementation on Zn to enhance a new method for copper removal from rinse water and waste water drained from electroplating industry.

Materials

Copper sulphate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (BDH) and sodium diethyldithiocarbamate (BDH) were used for the preparation of solutions for the experiment.

Kinetic measurements

CuSO_4 and deionized water were used to prepare the blank solution for Cu^{2+} (100 ppm) in the presence of four different concentrations of sodium diethyldithiocarbamate (25.689, 51.378, 77.067 and 102.755 ppm) at 25 °C.

Furthermore, to study the effect of temperature on the rate of cementation, the reaction rate was determined in the absence of the organic compound sodium diethyldithiocarbamate at four different temperatures; 25, 30, 35, 40 °C.

The zinc active surface was polished, then degreased with trichloroethylene, after that washed with alcohol and finally rinsed by deionized water. The zinc cylinder used in each run has a 9.0 cm length, 1 ml diameter and 3.75 cm radius. The reaction was performed in 500 ml glass beaker containing 400 ml $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

During the reaction, 1.0 ml of sample was taken from the proceeding reaction solution at different time intervals and diluted by 9.0 ml of deionized water. The copper ion concentration was measured by using Perkin-Elmer atomic absorption spectrophotometer (AAS).

Results and discussion

Effect of the initial concentration of Cu^{2+} ions on cementation

There is a direct relation between cementation rate and copper ion concentration i.e., the cementation rate increases with an increase in copper precipitation. This may be attributed to the fact that with increasing initial concentration of metal in the solution (Cu^{2+}), the deposited copper tends to pass from fine grained compact and barely porous structure to a coarse-grained porous structure which increases the roughness leading to an increase in mass transfer rates. The continued removal of copper ion with time indicates that the deposited copper layer is porous and allows copper ions diffusing through it to react with zinc.

For the circulating batch reactor used in the work, the mass transfer coefficient was calculated using the following equation (Elshazly, 2005):

$$V_s \ln(C_o/C) = kAt \quad (1)$$

where V_s is the volume of solution (ml), C_o and C are the initial concentrations of Cu^{2+} ion at 0 time and at any time (t) respectively (ppm), A is the zinc cylinder active surface (cm^2) and t is the time of reaction (min).

Figs. 1–4 show the relation between $\ln(C_o/C)$ and time for blank solution at different concentrations at 25, 30, 35 and 40 °C respectively. Figs. 1–4 give a straight-line pass with origin, which indicates that the reaction is first order. The mass transfer coefficient (k) was obtained from the slope of the above Eq. (1). The data are represented in Table 1. The dependence of the calculated mass transfer coefficient on the initial Cu^{2+} concentration is shown in Figs. 1–4 and Table 1.

For a given velocity of a solution, the mass transfer coefficient is noticed to increase with the increase in the initial Cu^{2+} concentration. This result is consistent with the previous studies carried out under different conditions. The cementation rate increases with the increase of the initial Cu^{2+} concentration, due to the following effects:

- (i) The active surface of zinc receives the copper ions Cu^{2+} from the used bulk solution during cementation by the following ways:
 - (1) Diffusion through the diffusion layer (δ) present at the active surface of zinc.
 - (2) Electrical migration due to the electrostatic attraction between copper ions Cu^{2+} which are positively charged and negative zinc anode where it is cemented over the active surface of zinc cathode. It is a fact that the rate of copper ion Cu^{2+} transferred by electric migration as well as the rate of diffusion through negatively charged zinc active surface increases with the increase in the concentration of the used bulk solution, leading to an increase in the mass transfer coefficient.
- (ii) The initial increase in Cu^{2+} concentration and the increase in the cathode area facilitate the deposition of the porous copper deposits. These lead to an increase in the mass transfer coefficient and the rate of cementation.

Effect of an organic compound, sodium diethyldithiocarbamate, on the cementation process

Cementation of copper is commercially important. Its application falls into decorative purposes, removal of toxic copper

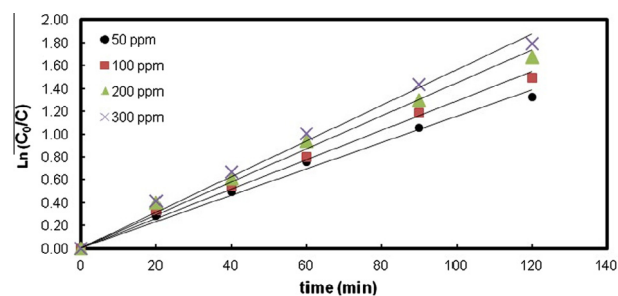


Figure 1 The relation between $\ln(C_o/C)$ and time for different Cu^{2+} concentration solutions at 250 rpm and at 25 °C.

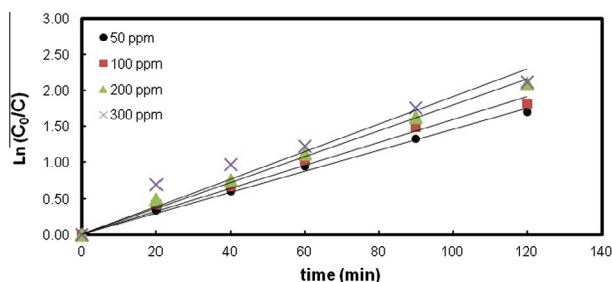


Figure 2 The relation between $\ln(C_0/C)$ and time for different Cu^{2+} concentration solutions at 250 rpm and at 30 °C.

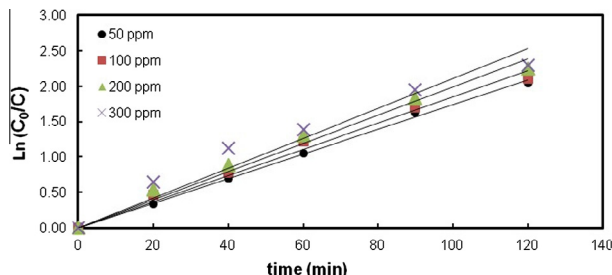


Figure 3 The relation between $\ln(C_0/C)$ and time for different Cu^{2+} concentration solutions at 250 rpm and at 35 °C.

ions and many others. Copper is generally cemented whether with additives or without them.

An organic additive was used to enhance the cementation process. The additive used is sodium diethyldithiocarbamate (NaDDC) because of its strong affinity for mercury, copper, nickel and zinc, it has been used in colorimetric determination of small quantities of copper and for its separation from other metals thus it works as a chelating agent.

[Keith et al., 1991]

Different concentrations of NaDDC and the dependence of the estimated mass transfer coefficient on the concentration of NaDDC were monitored (Table 2). It is clear that the cementation reaction rate increases with the increase in the concentration of the organic compound (see Fig. 5).

According to the obtained results from the reduction of Cu^{2+} on the active surface of a zinc cathode, we conclude the following:

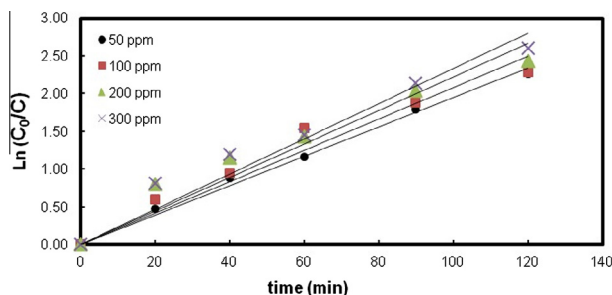


Figure 4 The relation between $\ln(C_0/C)$ and time for different Cu^{2+} concentration solutions at 250 rpm and at 40 °C.

Table 1 The calculated mass transfer coefficient values for copper ions Cu^{2+} concentrations at 250 rpm at different temperatures.

Temp. (°C)	Cu^{2+} conc. (ppm)	$k \times 10^2$ (cm s ⁻¹)
25	50	2.07
	100	2.26
	200	2.64
	300	2.83
30	50	2.64
	100	3.02
	200	3.40
	300	3.58
35	50	3.21
	100	3.40
	200	3.58
	300	3.96
40	50	3.58
	100	3.77
	200	4.15
	300	4.34

Table 2 The mass transfer coefficient values for the corresponding concentrations of NaDDC at 250 rpm and 25 °C.

NaDDC conc. (ppm)	$k \times 10^2$ (cm s ⁻¹)
25.689	3.584
51.378	3.773
77.067	4.150
102.755	4.527

- (i) The cementation rate of copper ions Cu^{2+} increased by increasing the concentrations of NaDDC.
- (ii) The percent of acceleration at different concentrations of the studied additive is calculated at 25 °C (Table 3). The acceleration percentage is calculated by the following equation (El-Gendy, 2014)

$$\% \text{ acceleration} = (k - k_o)/k_o \times 100 \quad (2)$$

where k_o = constant rate for blank solution, k = constant rate in presence of organic compound.

- (iii) The percentage acceleration increased by 58.58–100.31% depending on the concentration of NaDDC as shown in Fig. 6. The acceleration rate is expected to increase gradually with increasing NaDDC concentration until it reaches an equilibrium point.
- (iv) The acceleration of rate of reaction is due to: sodium diethyldithiocarbamate which reacts with Cu^{2+} solution giving a complex of copper diethyldithiocarbamate as shown in Scheme 1, so the copper sulphate concentration decreases (Jewsbury, 1953; Jankiewicz et al., 1999). Accordingly, the cementation rate and the mass transfer coefficient should increase by increasing the concentration of sodium diethyldithiocarbamate (Kompany-Zareh et al., 1999; Shar and Bhanger, 2002; Pang et al., 2007).

Table 3 The percentage acceleration of cementation reaction of Cu^{2+} solution containing different concentrations of NaDDC at 250 rpm and at 25 °C.

NaDDC conc. (ppm)	% Acceleration of NaDDC
25.689	58.58
51.378	66.93
77.067	83.62
102.755	100.31

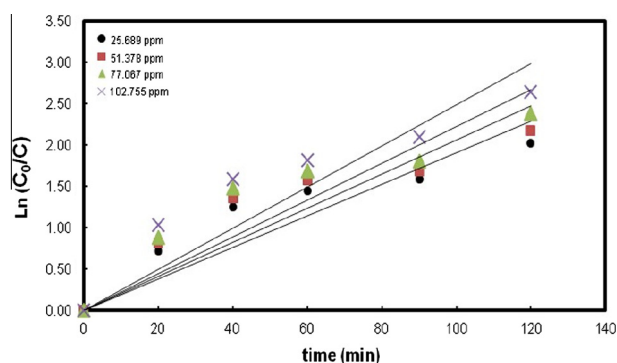


Figure 5 The graph between $\ln(C_0/C)$ versus time in the presence of different concentrations of sodium diethyldithiocarbamate (1.5 , 3.0 , 4.5 and 6.0×10^{-4} mol/l) or (25.689, 51.378, 77.067 and 102.755 ppm) for 100 ppm Cu^{2+} solution at 250 rpm and at 25 °C.

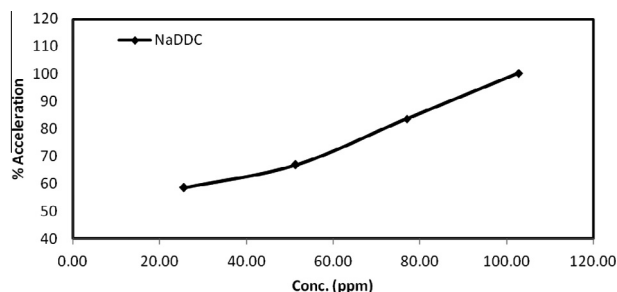
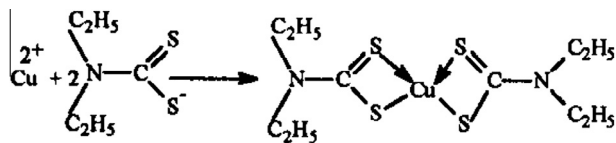


Figure 6 The relation between % acceleration and different concentrations of sodium diethyldithiocarbamate for 100 ppm Cu^{2+} solution at 250 rpm and at 25 °C.



Scheme 1 Reaction of copper (II) with diethyldithiocarbamate to form copper (II) diethyldithiocarbamate.

Conclusion

The cementation rate increases with the increase in copper ions Cu^{2+} concentration and temperature. The cementation rate of copper ions Cu^{2+} and the mass transfer coefficient

increase by increasing the concentration of sodium diethyldithiocarbamate (NaDDC) where sodium diethyldithiocarbamate reacts with Cu^{2+} solution giving a complex of copper diethyldithiocarbamate.

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